Supporting information

to

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Supramolecular P4VP-Pentadecylphenol Naphthalenebisimide Comb-Polymer: Mesoscopic Organization and Charge Transport Properties.

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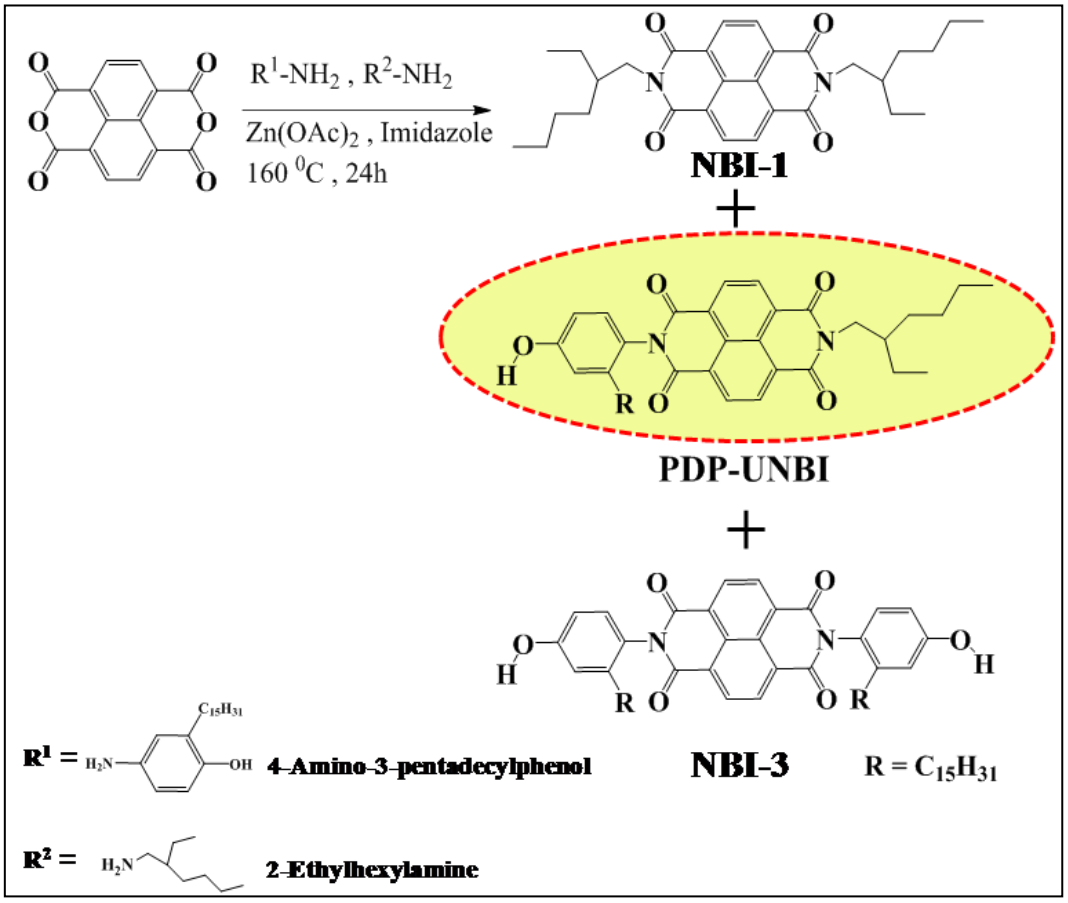
1. Materials and general information

Poly(4-vinylpyridine) (P4VP) (Mw =60,000) was purchased from Aldrich. It was dried in vacuum oven at 60 °C for 3 days prior to use. The other starting materials naphthalenetetracarboxylic acid dianhydride (NTCDA), 2-ethyl-1-hexyl amine, 3-pentadecylphenol and other reagents were also purchased from Aldrich and used without any further purification. All solvents used were of analytical grade and carefully dried before use according to standard procedures.

2. Synthesis

The synthesis strategy adopted for that of unsymmetrical pentadecylphenol naphthalenebisimide (**PDP-UNBI**) is outlined in Scheme-1 along with the corresponding reagents and reaction conditions.



Scheme-S.1. Synthesis of unsymmetrical naphthalenebisimide **PDP-UNBI** by statistical condensation with equivalent ratios of two amines.

(i) 4-amino-3-pentadecyl phenol. The synthesis was followed according to reported literature procedure.[1] Yield : 81%. ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm): 7.20 (d, 1H, Ar-H), 6.53-6.47 (m, 2H, Ar-H), 2.63 (t, 2H, Ar-C**H$_2$**-), 1.60 (t, 2H, Ar-CH_2-C**H$_2$**), 1.36–1.23 (b,

other aliphatic 24H), 0.86(t, 3H, Ar-$(CH_2)_{14}$-CH_3). ^{13}C NMR (50 MHz, $CDCl_3$, δ ppm): 146.8, 138.7, 126.2, 117.5, 113.4, 30.9, 29.5, 22.7, 14.3. FT-IR (KBr, cm^{-1}): 3432, 3350, 3296, 1647, 1585, 1416, 1334, 914, 675 cm^{-1}. MALDI-TOF MS (Dihydroxybenzoic acid matrix): m/z calculated for $C_{21}H_{37}NO$: 319.29; found 320.31$[M+1]^+$.

Synthesis of Unsymmetrical naphthalenebisimide (PDP-UNBI)

Naphthalene-1,4,5,8-tetracarboxylic dianhydride (2.0 g, 7.54 mmol) was heated in 25g molten imidazole reagent for half an hour followed by simultaneous addition of 4-amino-3-pentadecylphenol (2.37 g, 7.54 mmol) and 2-ethylhexylamine (0.962 g, 7.54 mmol) under nitrogen atmosphere. It was stirred at 160 °C for 12 hours in presence of catalytic amount of $Zn(OAc)_2$. The reaction mixture was then cooled to room temperature and stirred overnight with 250 mL 2N HCl. The precipitate was filtered, washed with water followed by methanol and dried at 120 °C. This crude product comprised of a mixture of 3 major components viz., symmetrically substituted ethylhexyl derivative (NBI-1), the unsymmetrically substituted naphthalenebisimide with ethylhexyl group on one imide position and 3-pentadecyl phenol (PDP) group on other side (NBI-2) named as PDP-UNBI and symmetrical PDP substituted NBI-3. The unsymmetrical PDP-UNBI was separated from this mixture by column chromatography on silica gel using $CHCl_3$/ MeOH mixture. The NBI-1 was eluted in 100% $CHCl_3$, PDP-UNBI in $CHCl_3$/ MeOH (99/1 v/v) and NBI-3 in $CHCl_3$/ MeOH (97/3 v/v).

(ii) N, N'-Bis-Ethylhexyl-naphthalene–1,4:5,8–tetracarboxylic bisimide (NBI-1): Yield : 35 %. ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm): 8.77(m, 4H, naphthalene ring), 4.14(m, 4H, imide-C**H**$_2$), 1.94(m, 2H, imide-CH_2-C**H**), 1.36 (broad multiplet, corresponding to other aliphatic protons), 0.96(2t, 12H, end C**H**$_3$ groups of ethyl hexyl tail).^{13}C NMR (50 MHz, $CDCl_3$,δ ppm): 163.3, 162.7, 153.5, 131.1, 129.2, 126.9,72.3, 70.8, 67.5, 59.1, 47.0, 37.0, 31.7, 29.3, 23.0, 14.1 FT-IR (KBr, cm^{-1}): 2939, 2850, 1709, 1659, 1600, 1578, 1512, 1446, 1336, 1255, 1183, 1086, 1024, 793, 745, 772, 708, 644. MALDI-TOF MS (Dithranol matrix): m/z calculated for $C_{30}H_{38}N_2O_4$: 490.28; found 491.31$[M+1]^+$.

(iii) N- (2-ethylhexyl) -N'- (4-hydroxy-2-pentadecylphenyl) naphthalene -1,4,5,8-tetracarboxylic acid bisimide -PDP-UNBI (NBI-2): Yield : 24 %. M.P.: 106 ^{0}C.^{1}H NMR (200 MHz, $CDCl_3$, δ ppm) : 8.82(m, 4H, naphthalene ring), 7.03–6.74 (3t, 3H, Ar**H**-PDP), 4.18 (m, 2H, imide-N-C**H**$_2$), 2.35 (t, 4H; Ar-C**H**$_2$), 1.96 (m, 1H, imide-N-CH_2-C**H**), 0.90-0.86 (m, 9H, end CH_3 of ethyl hexyl group + terminal C**H**$_3$ of C-15 alkyl chain), 1.51-1.0(other aliphatic protons). ^{13}C NMR (50 MHz, $CDCl_3$, δ ppm) : 163.3, 159.9, 158.3, 143.1,

139.6, 136.7, 135.2, 130.3, 129.8, 126.2, 124.9, 123.1, 122.6, 113.3, 106.2, 55.6, 32.7, 31.9, 29.9, 26.9, 22.8, 14.3. FT-IR (KBr, cm^{-1}): 3408, 3190, 3075, 2923, 2853, 1705, 1661, 1581, 1495, 1454, 1373, 1343, 1297, 1245, 1191, 1154, 1092, 1056, 982, 958, 874, 810, 771, 731, 702, 638. MALDI-TOF MS (Dithranol matrix): m/z calculated for $C_{43}H_{56}N_2O_5$: 680.42 ; found 681.38$[M+1]^+$. Elemental analysis calculated (%): C 75.85, H 8.29, N 4.11; found: C 75.74, H 8.36, N 3.67.

(iv) N,N'-Bis-(3-pentadecylphenyl)-naphthalene-1,4:5,8-tetracarboxylic bisimide (NBI-3) : Yield : 19 %. ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm: 8.87(dd, 4H, naphthalene), 7.07-6.79(3t, 6H, PDP-Ar**H**), 2.39 (t, 4H; PDP-Ar-C$\mathbf{H}_2$), 1.54(t, 4H; PDP-Ar-CH_2-C$\mathbf{H}_2$), 0.87 (m, 6H, terminal C$\mathbf{H}_3$ groups of C-15 alkyl chain), 1.24-1.13(other aliphatic protons). ^{13}C NMR (50 MHz, $CDCl_3$, δ ppm) : 162.4, 159.2, 158.6, 142.9, 139.8, 135.7, 135.2, 131.3, 129.7, 127.2, 125.1, 123.3, 122.8, 113.3, 106.2, 55.6, 32.7, 31.9, 29.9, 26.9, 22.8, 14.3.FT-IR (KBr, cm^{-1}): 3365, 2928, 2854, 1711, 1664, 1582, 1499, 1452, 1345, 1298, 1250, 1180, 1094, 979, 876, 839, 768, 643. MALDI-TOF MS (Dithranol matrix): m/z calculated for $C_{56}H_{74}N_2O_6$: 871.22 ; found 872.13$[M+1]^+$.

3. Structural characterization, purity analysis and thermal properties of (PDP-UNBI)

Figure-S.1. ^{1}H-NMR spectra of the naphthalenebisimide derivatives NBI-1, **PDP-UNBI** and NBI-3 recorded in $CDCl_3$ at room temperature.

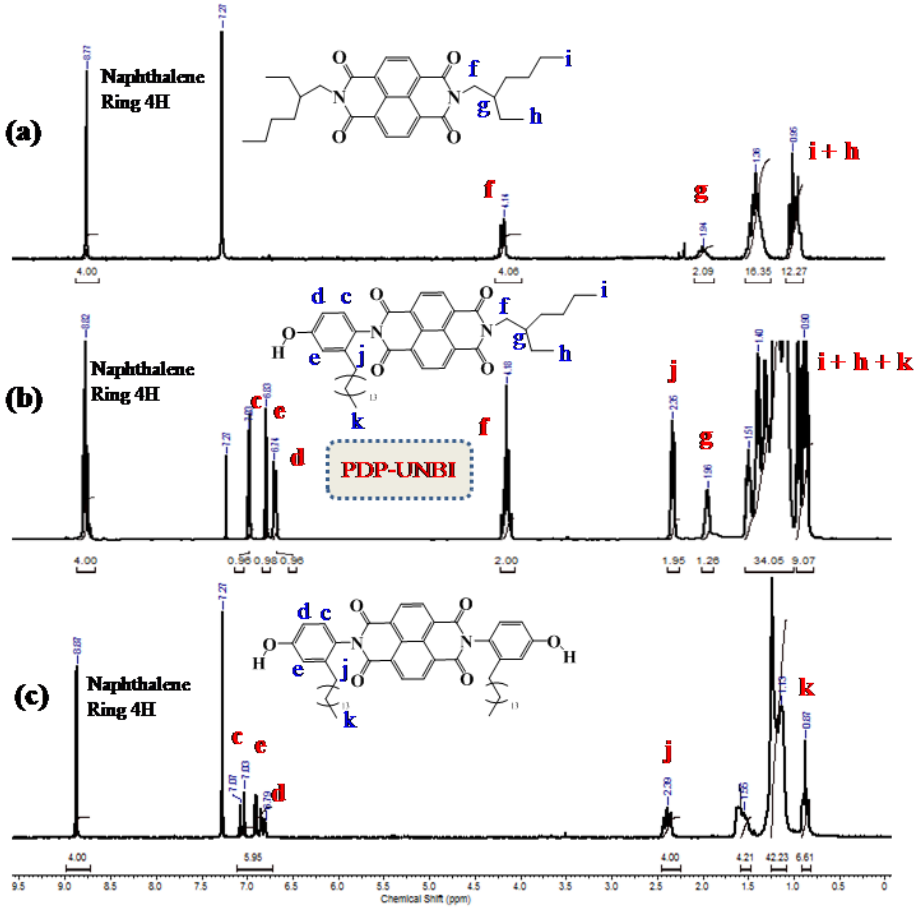


Figure-S.2. MALDI-TOF spectra of the unsymmetrical naphthalenebisimide **PDP-UNBI.**

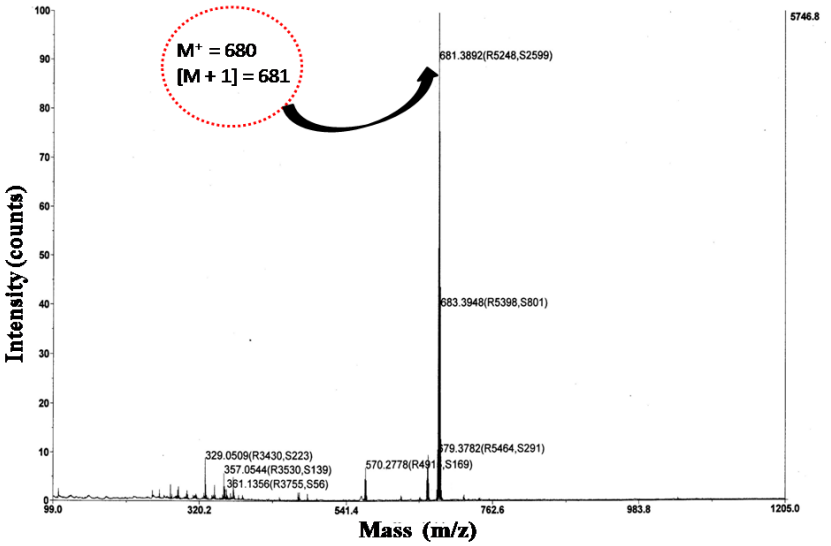


Figure-S.3. Size exclusion chromatogram of **PDP-UNBI** run using THF solvent.

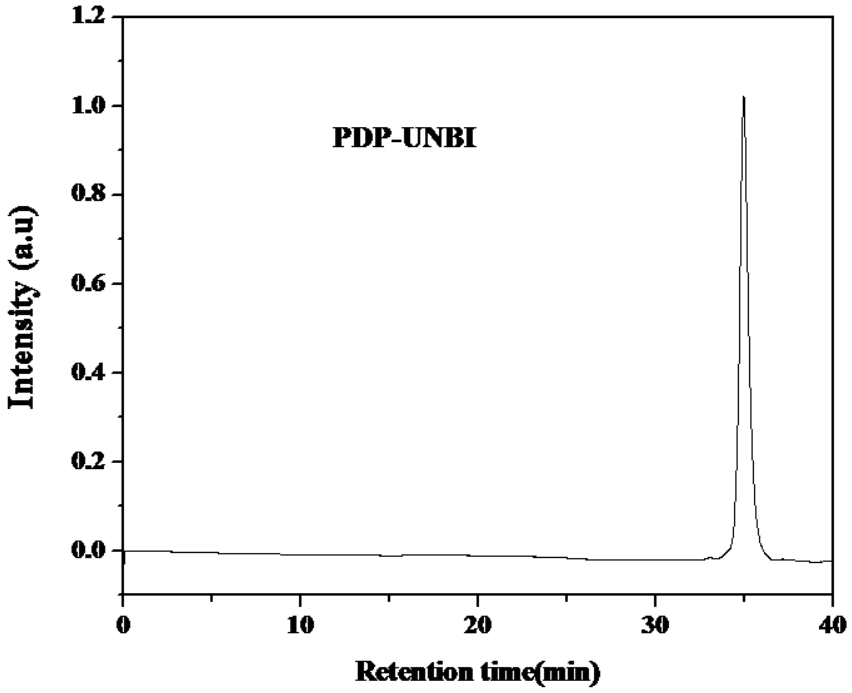


Figure-S.4. TGA thermogram of **PDP-UNBI** with the 10 % weight loss temperature.

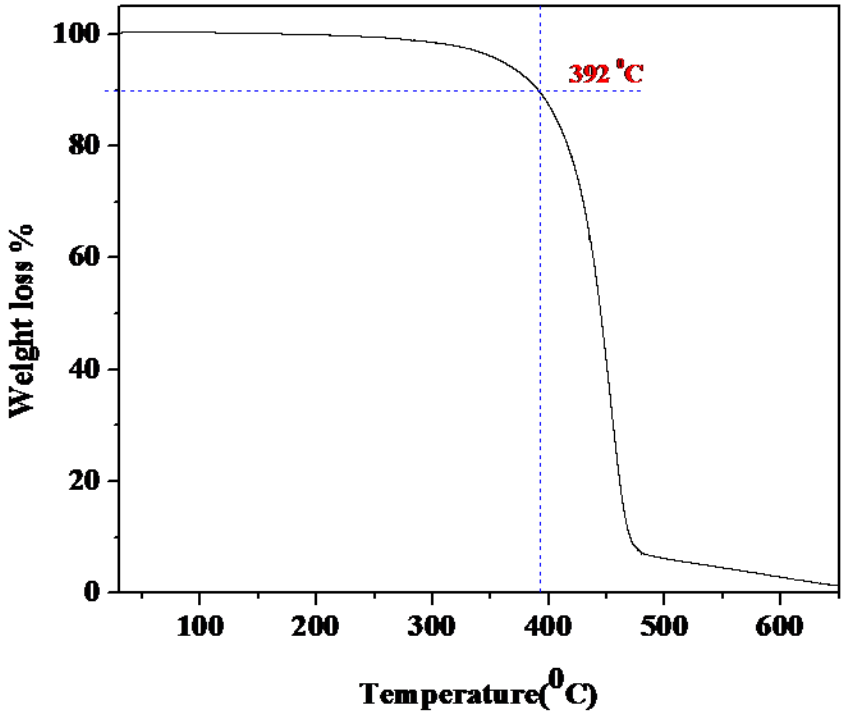


Figure-S.5. DSC profile of **PDP-UNBI** showing the second heating and first cooling cycles.

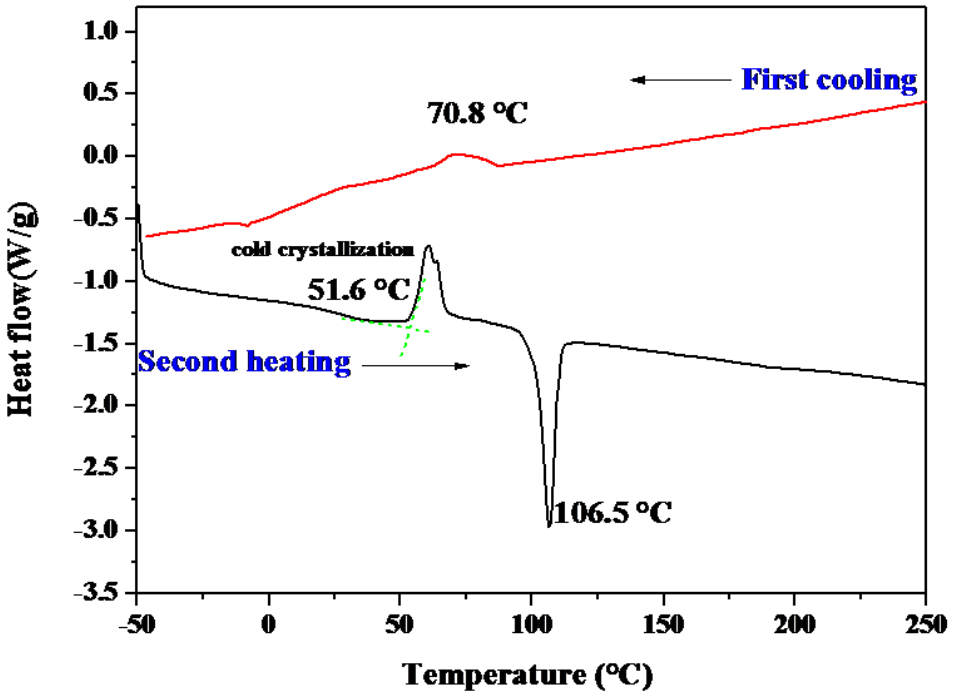


Figure-S.6. FT-IR spectra of P4VP, **PDP-UNBI** and **P4VP(PDP-UNBI)$_n$** (n = 0.25,0.50, 0.75 and 1.00) in the regions (a) 1020 to 990 cm^{-1} and (b) 1430 to 1390 cm^{-1}.

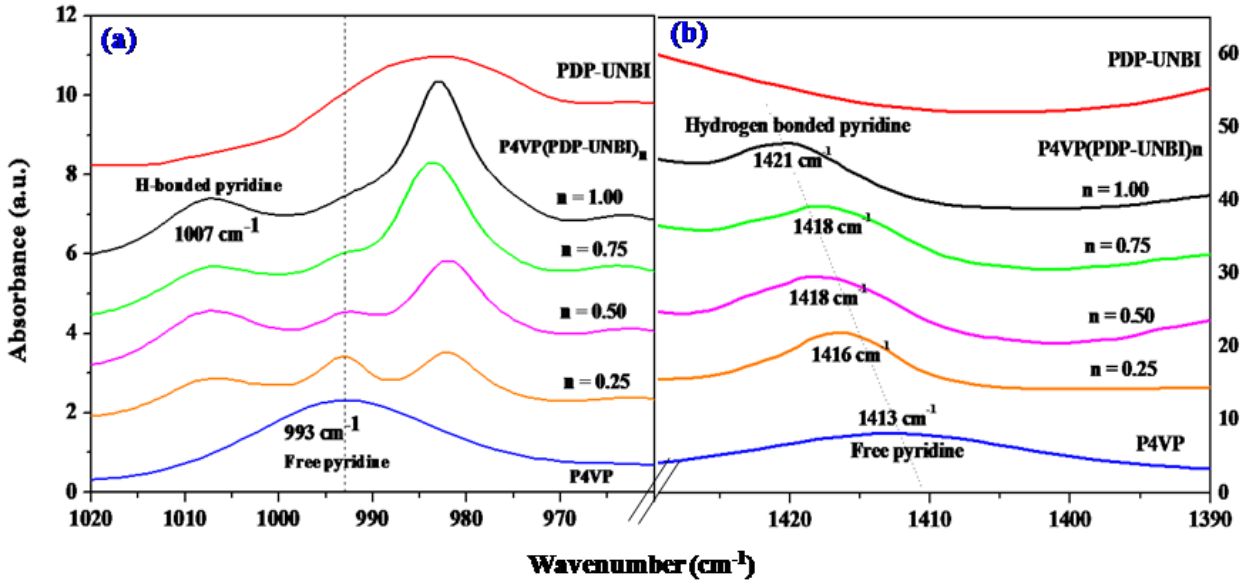


Figure-S.7. Expanded aromatic region of ^{1}H-NMR spectra of **P4VP(PDP-UNBI)$_n$** recorded in $CDCl_3$ at a concentration of 5 mg/mL in deuterated chloroform ($CDCl_3$) at room temperature as a function of n = 0.25, 0.50, 0.75, 1.00.

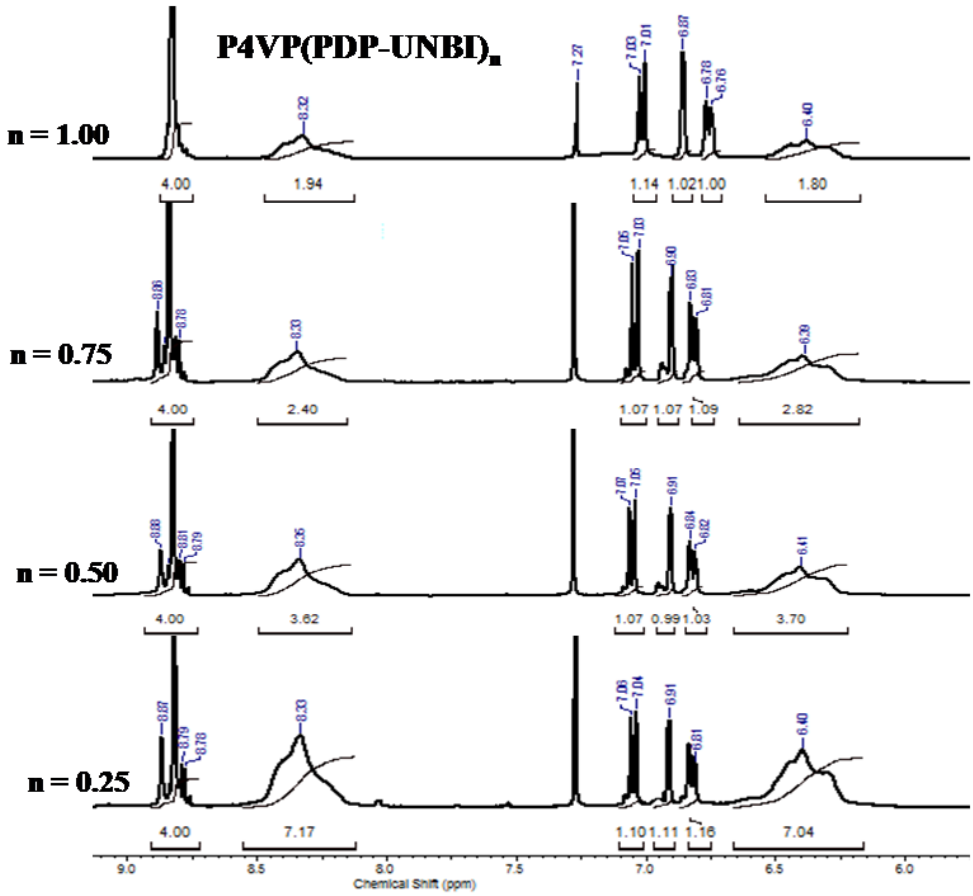


Figure-S.8. Normalized WXRD trace from 2θ = 5 -35° of (A) **EH-SNBI** and **P4VP(EH-SNBI)$_{1.0}$** (B) **PDP-UNBI** and **P4VP(PDP-UNBI)$_{1.0}$** recorded at room temperature.

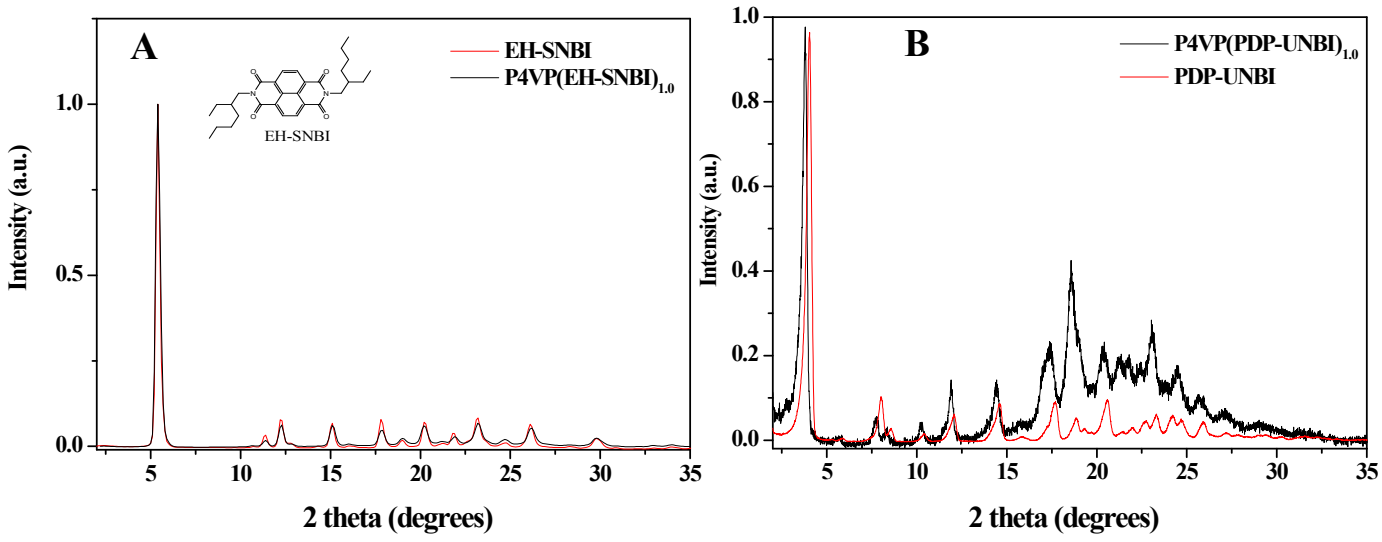


Figure-S.9. Optical microscopy images of thin and needle-like **PDP-UNBI** single crystals grown from DMF solution.

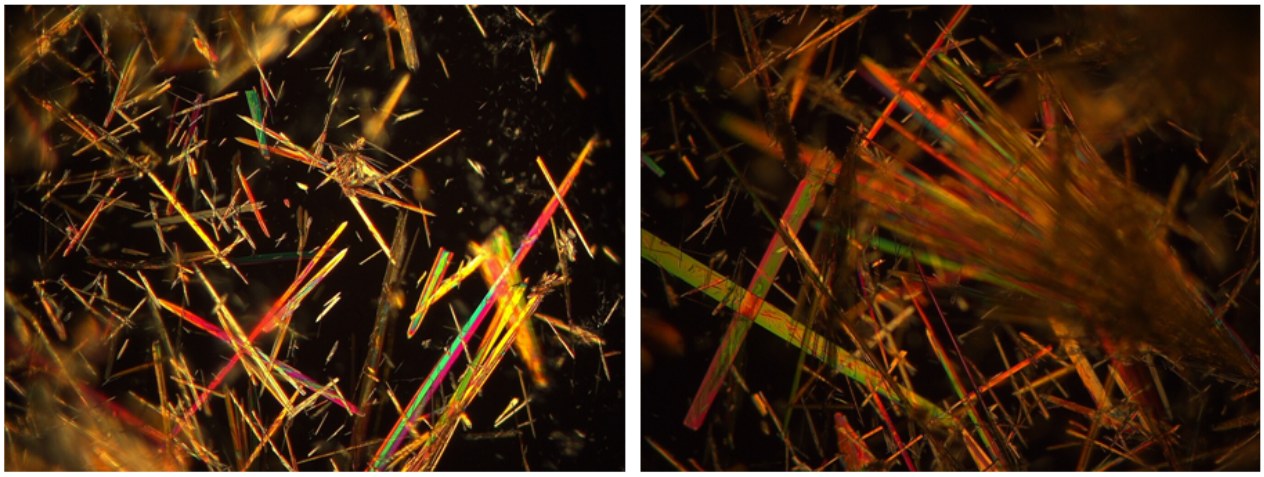


Table-S.1. Crystallographic data and Structure refinement summary.

Compound	**PDP-UNBI** (phenol)
Empirical formula	$C_{43}H_{56}N_2O_5$
Crystal color, habit	Yellow thin needles
Preparation	Recrystallization from DMF
Temperature	100 K
Crystal system	Orthorhombic
Space group	Iba2
Unit cell dimensions	a = 20.076(8) Å b = 49.223(19) Å c = 8.695(3) Å α = β = γ = 90°
Volume	8592(6) $Å^3$
Density (calculated)	1.096 Mg/m^3
Z	8
Theta range for data collection	0.83 to 22.14°
Reflections collected	44362
Independent reflections	5240 [R(int) = 0.1967]
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.526
R-factor	12 %

Figure-S.10. Packing structure of **PDP-UNBI** viewed through c-axis showing the hydrogen bonding with one DMF molecule co-crystallized per PDP unit (yellow dotted box) and the next closest contact for H-bonding possible between PDP-phenol and imide carbonyl of nearest naphthalene ring (red dotted circles).

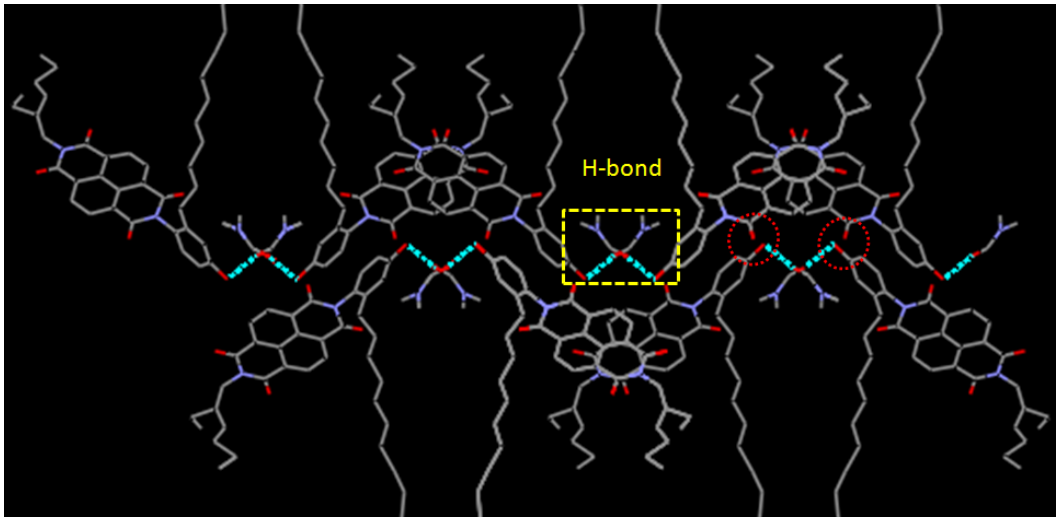
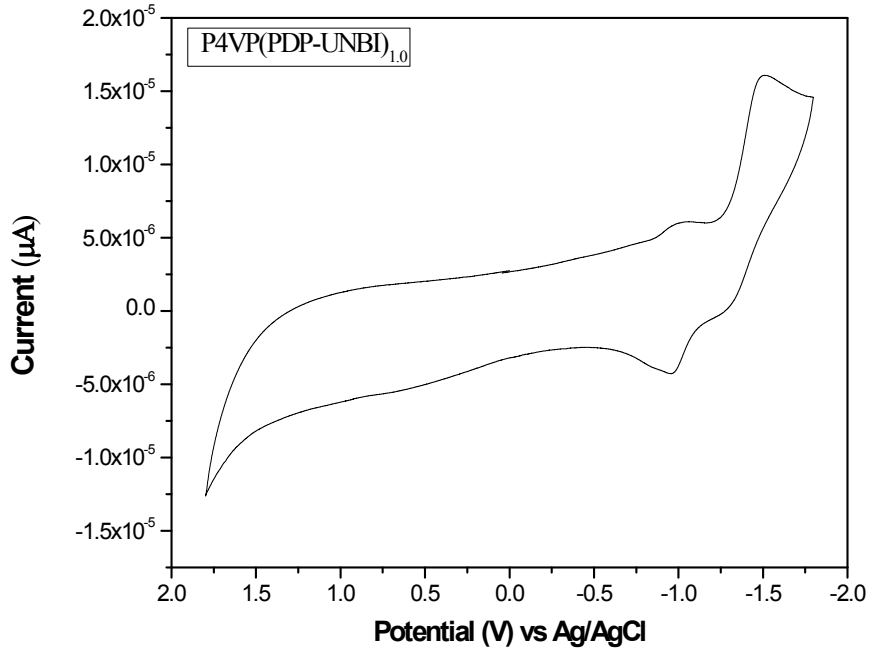


Figure-S.11. Cyclic voltammetry data for the **P4VP(PDP-UNBI)$_{1.0}$** supramolecular complex.



Calculation of HOMO-LUMO values

From Cyclic voltammetry:

$E_{1/2}$ = 75 mV

E_{LUMO} = -[-0.669 - 0.075 + 4.8]

= - 4.056 eV

Bandgap from absorption spectra = 3.08eV

E_{HOMO} = -[BG – E_{LUMO}]

= -[3.08 – (-4.06)]

= -7.14 eV

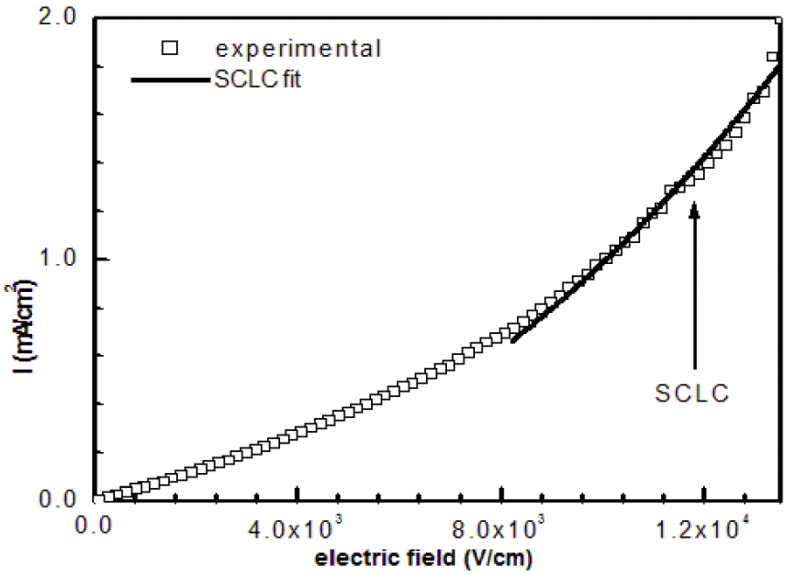
E_{LUMO} = - 4.06 eV ; E_{HOMO} = - 7.14 eV

11. Literature :

1) S. B. Mhaske, R. V. Bhingarkar, M. B. Sabne, R. Mercier, S. P. Vernekar, J. Appl. Polym. Sci. 2000, 77, 627.

Figure-S12. Current density vs field plot for (a) **P4VP(PDP-UNBI)$_{1.0}$** (thickness ~ 5.3 μm, area ~ 0.15 cm^2) and (b) **PDP-UNBI** (thickness ~ 4.4 μm, area ~ 0.094 cm^2) with the solid line indicating the SCLC fit.

(a)



(b)